BASF-Aerospace/Georgia Tech Electrochromics Program

- Final Report

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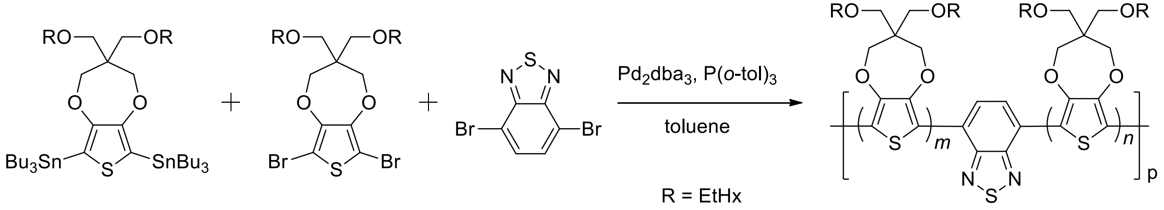
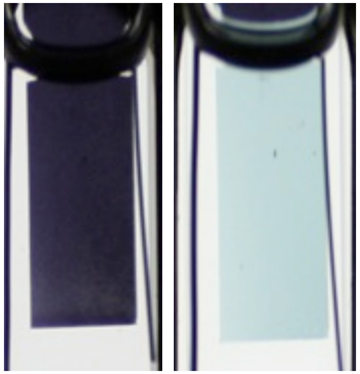
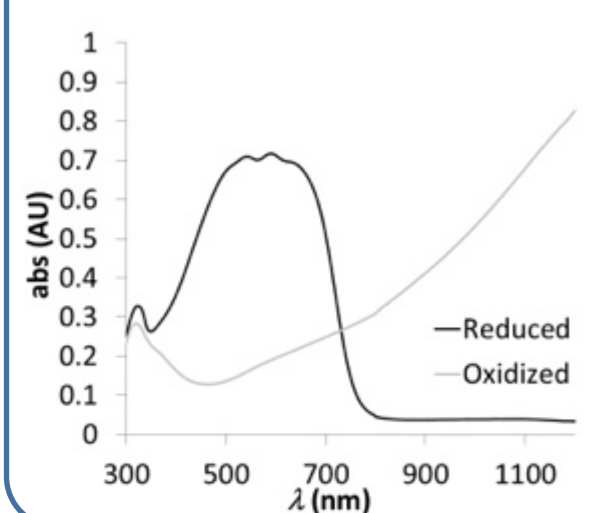
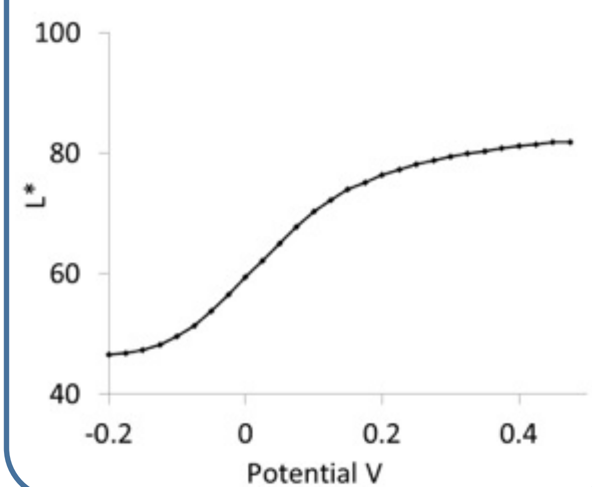
ECP Black: Overview

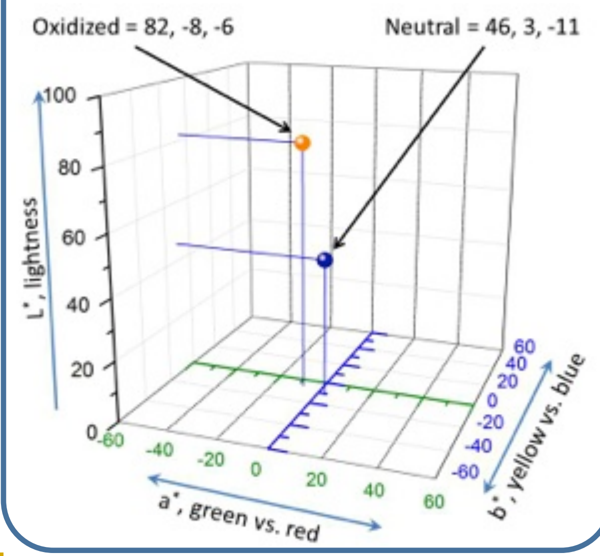
Preparation: Pd Catalyzed Stille Cross-coupling







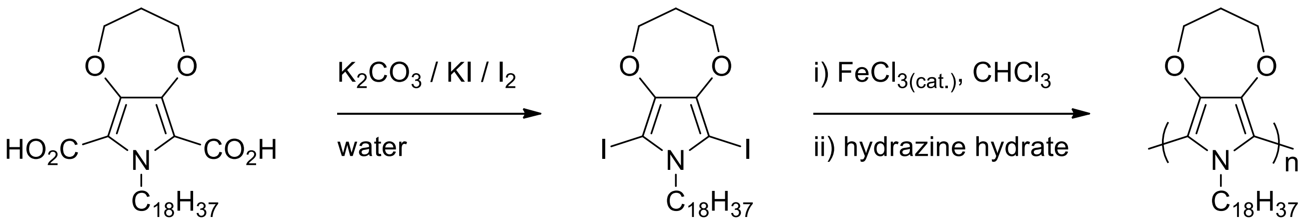




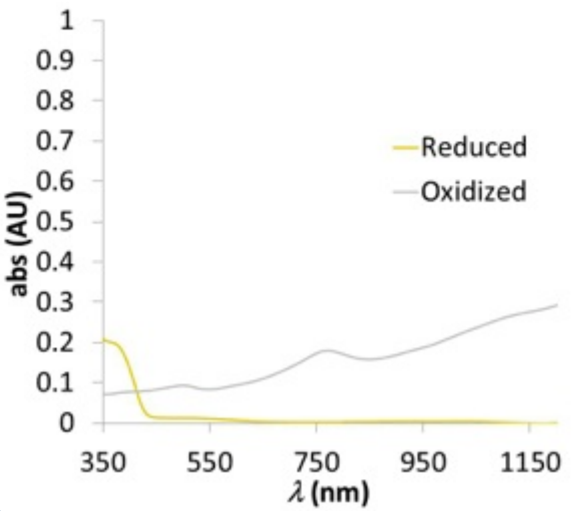
Previous film characterization data

MCCP: Overview

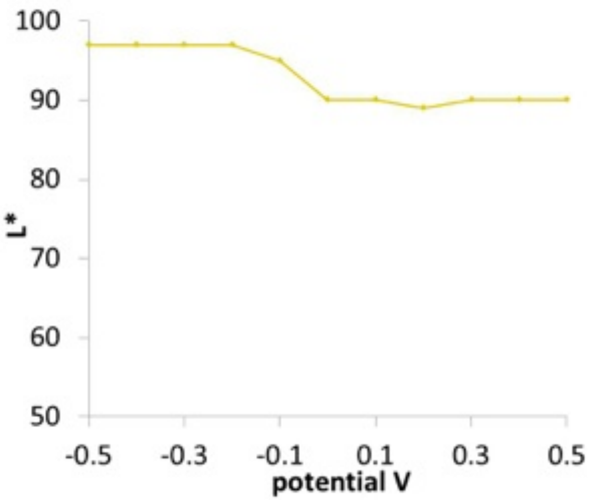
Preparation: Iodo-decarboxylation / de-iodination polymerization



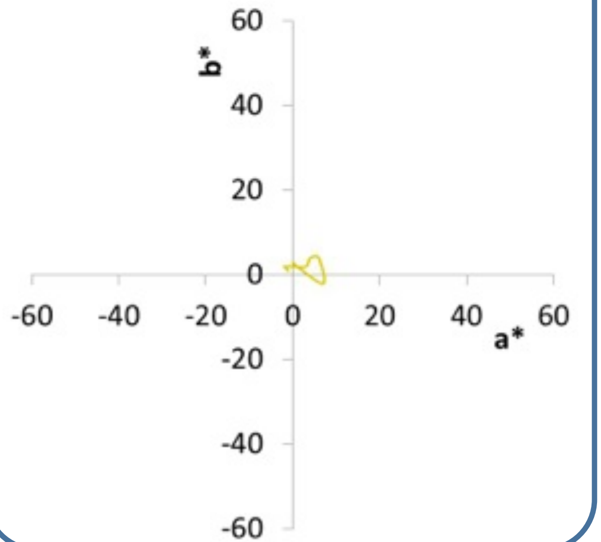
UV-vis –NIR Spectra



L* *vs* potential



a b** color track



Previous film characterization data

ECP-Black films of high OD

Status

Films of increasing OD were spray-cast from solution onto ITO/glass (0.3”x 2”, R_s = 5-15 Ω/sq). The films were electrochemically switched in 0.5 M LiBTI/Propylene carbonate electrolyte. These experiments were performed to understand the limits of spray-cast film thicknesses and the highest optical density achievable in a stable film switched in a liquid electrolyte and resulting bleached-state transmittance.

The dry-film absorbances at 555nm were 0.7, 1.3, 1.5, 2.0.

Research Activities

The films that were sprayed to absorbances greater than 2.0 tended to crack and peel from the electrode during electrochemical switching.

The thickest film (abs = 2.0) had an average %T (in the range of 580-620 nm) of 1.2% achieving an average %T of 27.7% in the bleached state. As expected, the film that reached the highest bleached state %T (72.0%), had the highest dark state %T (29.7%).

However, the film with the dry absorbance value of 1.3 had a bleached state transmittance of 51% and a dark state transmittance of 15%.

Film Spectra and Colorimetry

Figure : ECP-Black films of increasing thickness in colored states

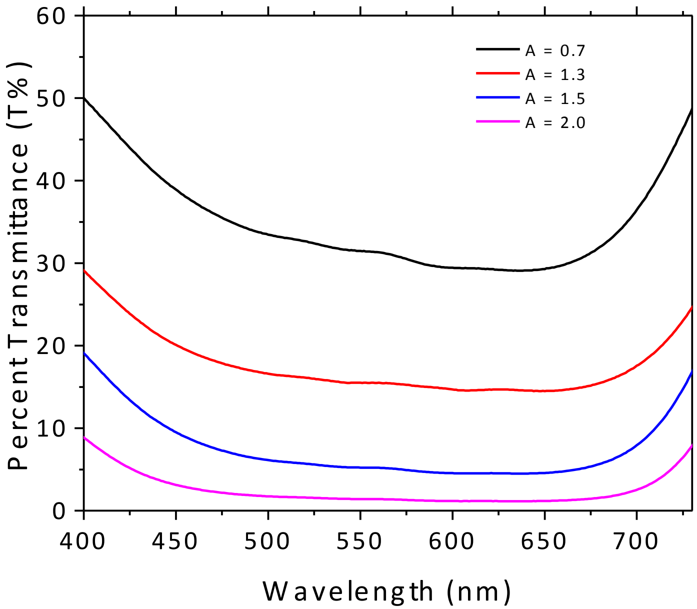
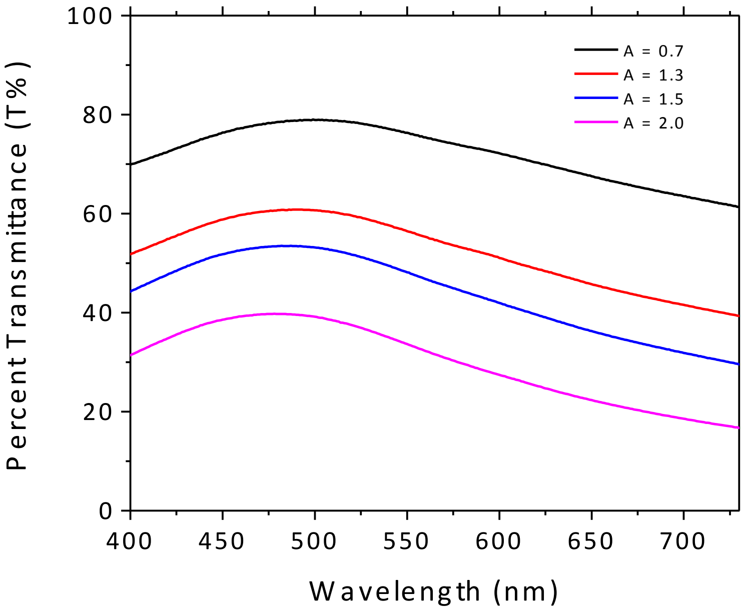


Figure : ECP-Black films of increasing thickness in bleached states



Dry Film Abs	Δ%T	$\%T_{580\text{-}620}$ Colored	$\%T_{580\text{-}620}$ Bleached	ΔL*	L* Colored	L* Bleached	a*,b* colored	a*,b* bleached
0.7	42.3	29.7	72.0	24.1	64.5	88.6	0.8, -8.2	-4.0,-1.3
1.3	35.9	15.0	50.9	40.8	34.3	75.1	2.8, -12.3	-7.4, -5.1
1.5	37.0	4.7	41.7	45.7	25.8	71.5	3.4, -13.4	-8.2, -4.5
2.0	26.5	1.2	27.7	48.1	15.2	63.3	5.3, -9.6	-9.4, -6.1

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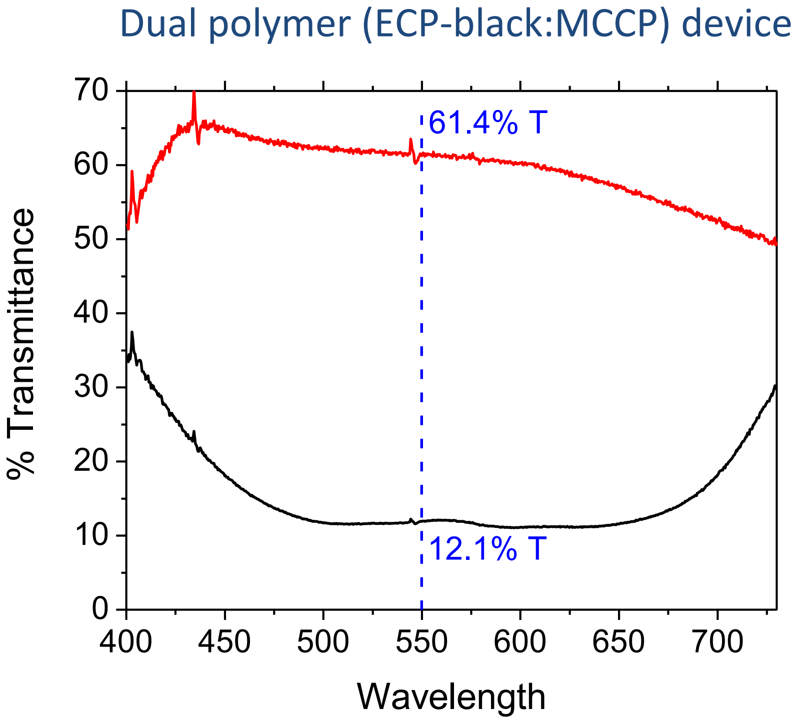
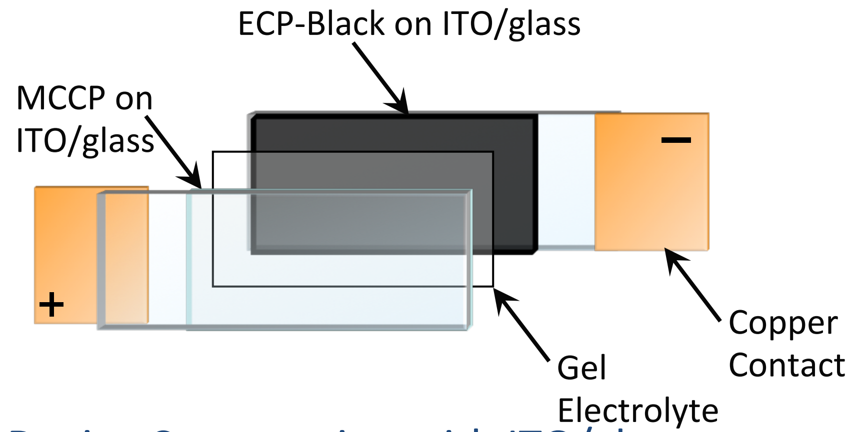
Film Spectra Measured with Varian Cary UV/Vis-NIR Spectrophotometer
Film Colorimetry Measured with Minolta Colorimeter

ECP-Black Dual Polymer Devices





- Standard Device Construction with ITO/glass electrodes (5-10 Ω/sq)
- Gel electrolyte comprised of LiBTI, PMMA, PC
- Adco PIB edge sealant used and devices constructed in Ar-drybox
- ECP-black sprayed to varying thicknesses with charge balance maintained from film of MCCP

- Determined that while the high optical density required (<0.8%T) can be reached, there are limitations to the bleached state transmittance (>65% T) with using ECP-black in standard dual polymer ECD

ECP-Black ECDs of high OD—Non-optimized charge balance

Status

Films of increasing OD of ECP-Black (1.1 abs to 3.8 abs) were spray-cast from solution onto ITO/glass (1”x 1.5”, R_s = 5-15 Ω/sq). Films of constant OD of MCCP (~0.5 abs at 300 nm) were sprayed onto similar ITO/glass. The electrolyte utilized was 0.5M LiBTI, 20wt% PMMA, PC. The devices were cycled several times to break in, followed by electrochemical, optical, and colorimetric characterization.

Research Activities

Unlike in the films switching in liquid electrolyte, the devices of highest optical density did not peel and crack. These were the first sets of devices made by the UF team and several either did not switch or stopped switching after a few cycles. As the team has become more experienced, the success rate has increased.

This first step of non-optimized devices shows that while a high OD of ECP-black can be obtained, the bleached state %T is low. These results show that the use of a higher viscosity electrolyte stabilizes the film on the electrode, but does not improve device contrast. We have demonstrated that the high optical density desired by Boeing can be obtained. Next steps involve optimizing the amount of MCCP as it is known that effective charge balance in a dual polymer ECD is necessary for optimal device performance.

ECP-Black ECDs of high OD—Non-optimized charge balance

Device Number	Dry Film Abs	$\%T_{580\text{-}620}$ Colored	$\%T_{580\text{-}620}$ Bleached	Min $\%T_{colored}$ (@517nm)	Max $\%T_{bleached}$ (@529nm)	L* Colored	L* Bleached
3	Black A=1.1, MCCP A=0.6	6.4	14.6	5.0	16.6	35.6	64.9
5	Black A=1.4, MCCP A=0.5	2.3	22.9	2.8	28.0	N/A	N/A
6	Black A=1.4, MCCP A=0.5	2.8	23.5	3.3	24.5	N/A	N/A
7	Black A=2.3, MCCP A=0.5	0.45	20.3	0.7	26.2	8.5	48.3
10	Black A=3.0, MCCP A=0.6	0.1	5.7	0.17	8.1	4.7	37.6
12	Black A=3.8, MCCP A=0.7	0.04	2.8	0.03	4.9	3.6	23.5

Figure : Dark state transmittance spectra of ECP-Black:MCCP ECDs of increasing of ECP-Black with constant MCCP.

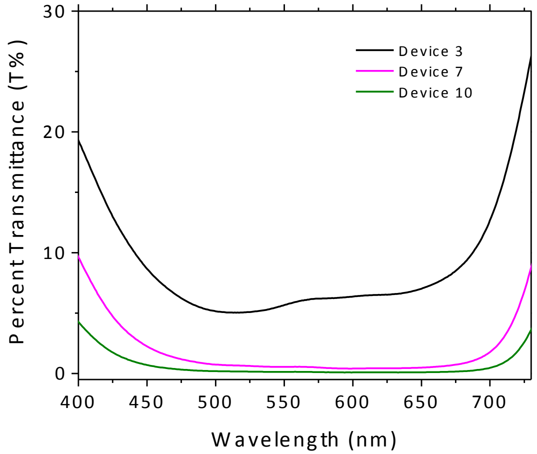
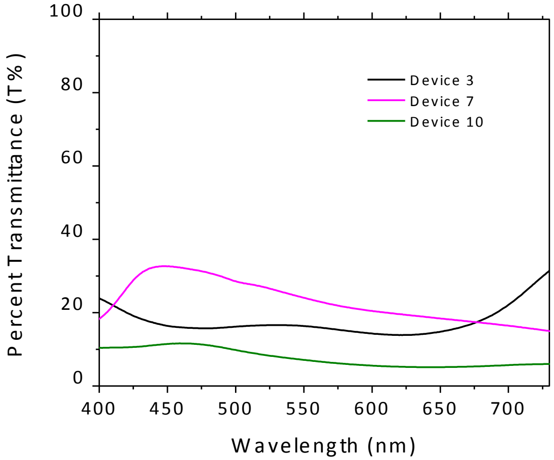


Figure : Bleached state transmittance spectra of ECP-Black:MCCP ECDs of increasing of ECP-Black with constant MCCP.



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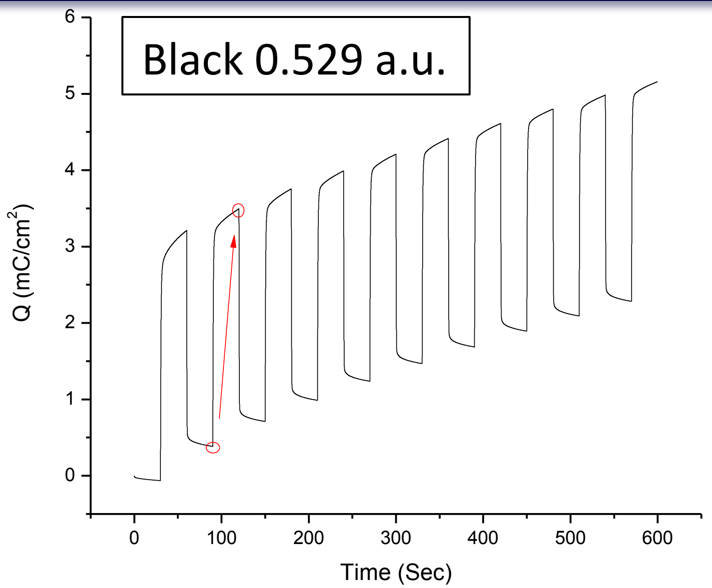
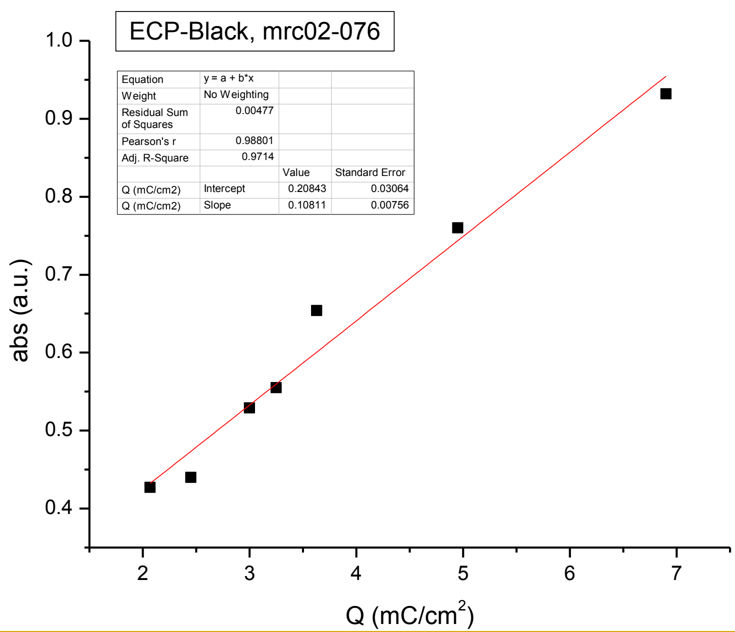
Device Spectra Measured with Varian Cary UV/Vis-NIR Spectrophotometer
Device Colorimetry Measured with Minolta Colorimeter

Optimizing charge balance -- ECP-Black Charge-to-Switch

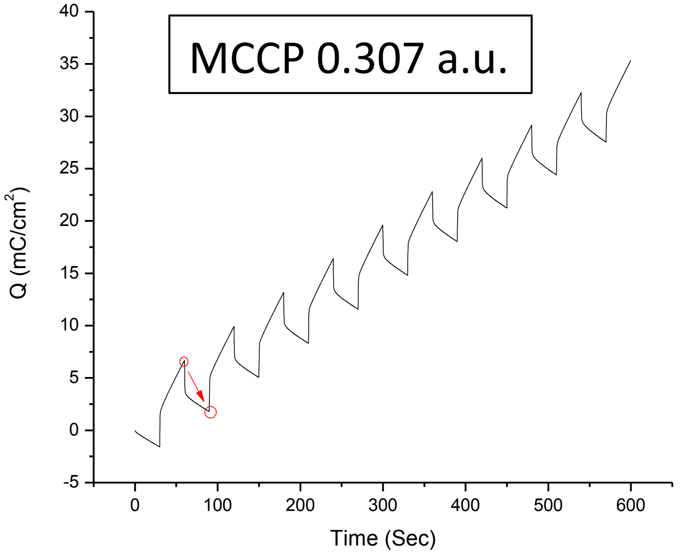


- Difference between two red circles gives the amount of charge necessary to bring an ECP-Black film to its charged state.
- The difference is then matched to the film's absorbance to help generate a calibration curve.

- The linear regression provides a way to estimate the charge density, Q_d, of ECP-Black at a given absorbance.
- This value is the charge necessary to switch the film from the neutral (colored) state to the oxidized (bleached) state.

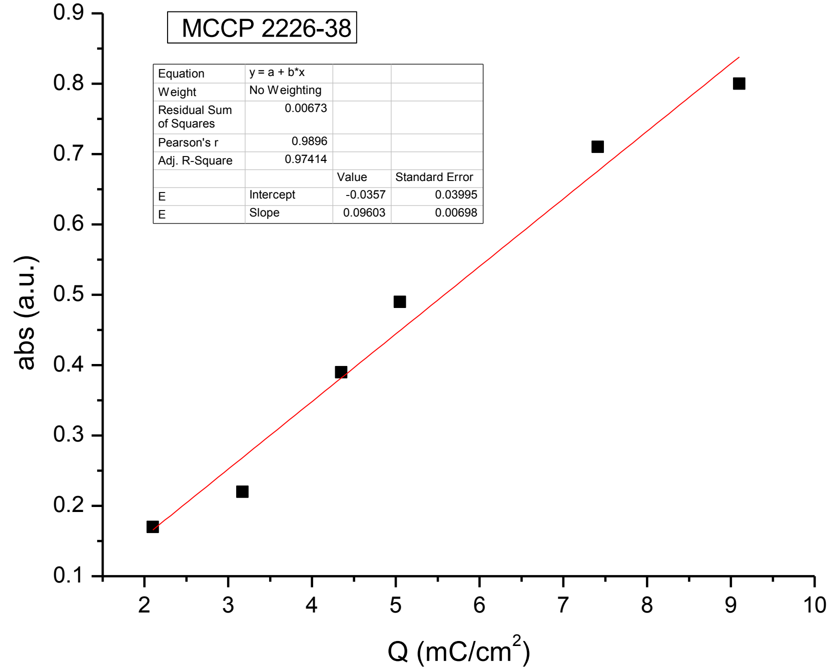


Optimizing Charge Balance-- MCCP Charge-to-Switch



- Charging of ECP-Black film must be matched by discharging of the MCCP film.
- The difference between the two red circles gives the amount of charge necessary to discharge MCCP.

- The linear regression provides a way to estimate the surface charge density, Q_d, of MCCP at a given absorbance.
- This value is the charge necessary to switch the film from the oxidized state to the neutral state.



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Charge-to-Switch Optimization Results

- By knowing the absorbance of one film, one can estimate the charge necessary to oxidize this film and use this charge to, in turn, find the absorbance to which you must spray the charge-balancing film for a device.

For example, for an ECP-Black film of 0.800 a.u.:

Black 0.800 a.u. $\rightarrow$ 5.4 mC/cm^2 $\rightarrow$ **MCCP 0.49 a.u.**

- Focus can then be towards constructing device structures with a variety of ECP-Black film thicknesses and closely matching the MCCP thickness to the ideal charge-match
- Parameters measured are: device contrast, switch speed, energy/power requirements, and lifetime.

High OD ECDs-Optimization of Charge Balance

Status

Films of constant OD of ECP-Black (2.0 abs, 1%T) were spray-cast from solution onto ITO/glass (1”x 1.5”, R_s = 5-15 Ω/sq). Films of increasing OD of MCCP (~0.5-1.1 abs at 300 nm) were sprayed onto similar ITO/glass. The electrolyte utilized was 0.5M LiBTI, 20wt% PMMA, PC. The devices were cycled several times to break in, followed by electrochemical, optical, and colorimetric characterization.

Research Activities

While the ratio of ECP-black to MCCP does not seem to have an large effect on the dark state transmittances, the effect on the bleached state is quite apparent. Devices with an ECP-black absorbance of 2.0 at the λ_{max} of 555nm and MCCP with an absorbance of 1.0 at a λ_{max} of 300nm gave the best contrast and closest to the desired transmittance values (1.2% to 34.2% in the range of 580-620nm). It is also apparent that the switching voltage range has an effect on the device switching parameters. From this data, we feel that the ECP-black:MCCP absorbance ratio of 2:1 is ideal and confirms the charge-to-switch experiments.

High OD ECDs-Optimization of Charge Balance

Device Number	Dry Film Abs	Voltage Range	$\%T_{580-620}$ Colored	$\%T_{580-620}$ Bleached	Min $\%T_{color}$ @594nm	Max $\%T_{bleach}$ @442nm	L* Colored	L* Bleached
1	Black A=2.2 MCCP A=0.5	-1.4/2.0	1.3	29.5	1.3	37.2	12.7	62.8
2	Black A=2.2 MCCP A=0.5	-1.4/1.6	1	31.3	1.0	40.9	10.0	65.5
3	Black A=2.0 MCCP A=0.8	-1.4/1.4	1.5	24.8	1.5	32.5	13.8	59.9
4	Black A=2.1 MCCP A=0.8	-1.4/1.6	1.6	31.9	1.6	39.3	14.2	65.7
5	Black A=2.1 MCCP A=1.1	-1.4/1.4	1.1	32.4	1.1	41.6	11.0	65.8
6	Black A=2.2 MCCP A=1.1	-1.4/2.0	1.2	34.2	1.1	39.5	11.0	67.2
7	Black A=2.0 MCCP A=1.3	-1.4/2.0	0.9	30.1	0.9	35.8	8.7	63.3
8	Black A=2.1 MCCP A=1.1	-1.4/1.6	1.7	26.6	1.7	35.3	12.0	61.1

Device Spectra and Colorimetry Measured with Optronics Spectroradiometer

High OD ECDs-Optimization of Charge Balance

Figure : Dark state transmittance spectra of ECP-Black:MCCP ECD of increasing MCCP with constant ECP-Black.

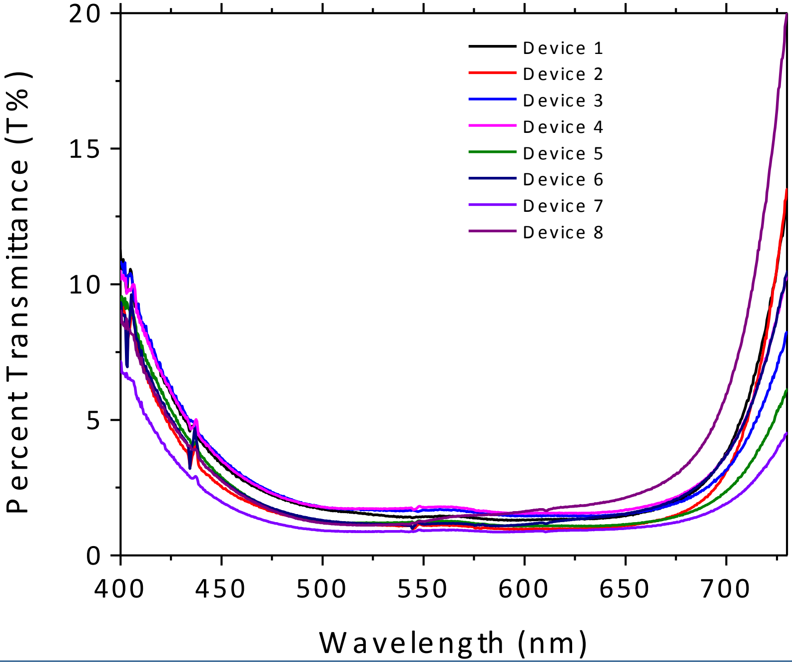
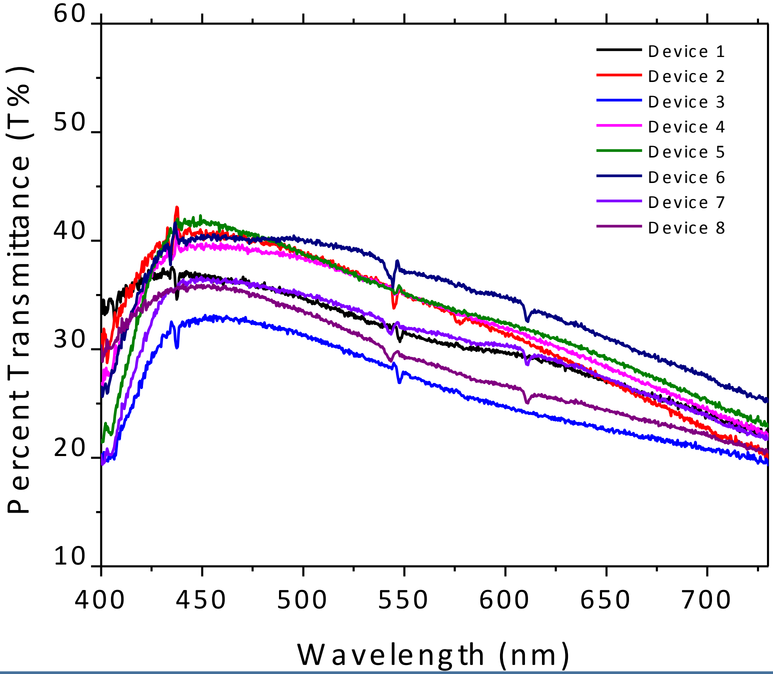


Figure : Bleached state transmittance spectra of ECP-Black:MCCP ECD of increasing MCCP with constant ECP-Black.



Device 1: Black A=2.2, MCCP A=0.5
Device 2: Black A=2.2, MCCP A=0.5
Device 3: Black A=2.0 MCCP A=0.8
Device 4: Black A=2.1 MCCP A=0.8

Device 5: Black A=2.1, MCCP A=1.1
Device 6: Black A=2.2, MCCP A=1.1
Device 7: Black A=2.0, MCCP A=1.3
Device 8: Black A=2.1, MCCP A=1.1

High OD ECDs-Optimization of 0.4 in^2 Devices

Status

With the ideal ratio of ECP-black to MCCP (based on optical absorption at the respective polymer film λ_{max}) found to be 2:1, additional devices were fabricated for further optical measurements that include spectral transmittance, colorimetry, lightness, and switching speeds as measured by transmittance

Research Activities

Again, while the devices did not demonstrate the bleached state transmittance as-desired, the colored state transmittance was sufficiently dark. Additionally, the device switching kinetics was measured optically and the devices were found to attain an optical state that within 2% of the full optical switch in under 60 seconds. Such a small change is not seen by the eye, and in fact, the device is perceived to reach a fully switched state within a matter of seconds.

High OD ECDs-Optimization of 0.4 in^2 Devices

Device Number	Dry Film Abs	%T $_{580\text{-}620}$ Colored	%T$_{580\text{-}620}$ Bleached	Min %T$_{color}$ @ 600 nm	Max %T$_{bleach}$ @ 435 nm	L* colored	L* Bleached
1	Black A=1.0 MCCP A=0.5	11.1	60.1	11.1	65.5	41.0	82.5
2	Black A=1.0 MCCP A=0.5	8.6	56.7	8.6	61.8	36.7	80.8
3	Black A=1.0 MCCP A=0.8	9.7	47.2	9.7	55.7	37.2	76.1
4	Black A=2.0 MCCP A=1.0	1.5	28.6	1.5	38.7	13.4	63.0
5	Black A=2.0 MCCP A=1.0	1.8	21.9	1.8	32.7	13.2	57.9
6	Black A=2.0 MCCP A=1.1	1.2	21.6	1.2	32.1	10.1	57.5

High OD ECDs-Optimization of 0.4 in^2 Devices

Figure : Dark state transmittance spectra of 0.4 in^2
ECP-Black:MCCP ECDs

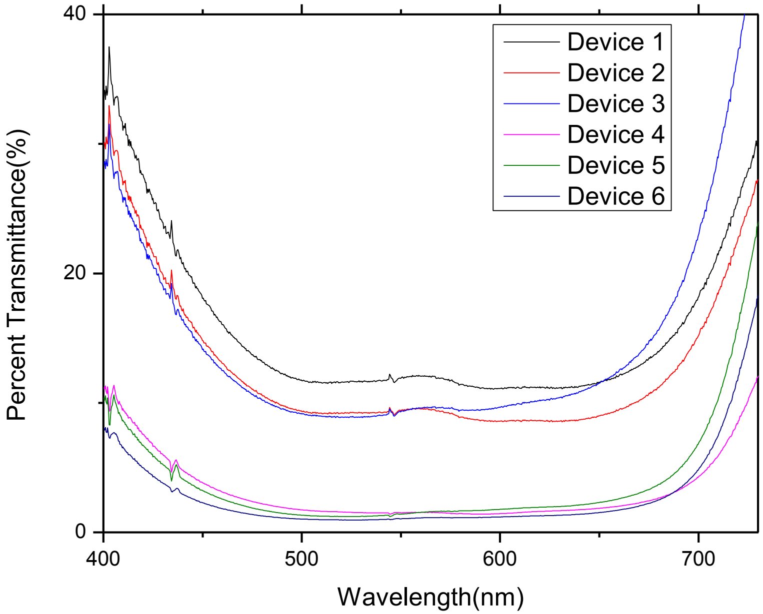
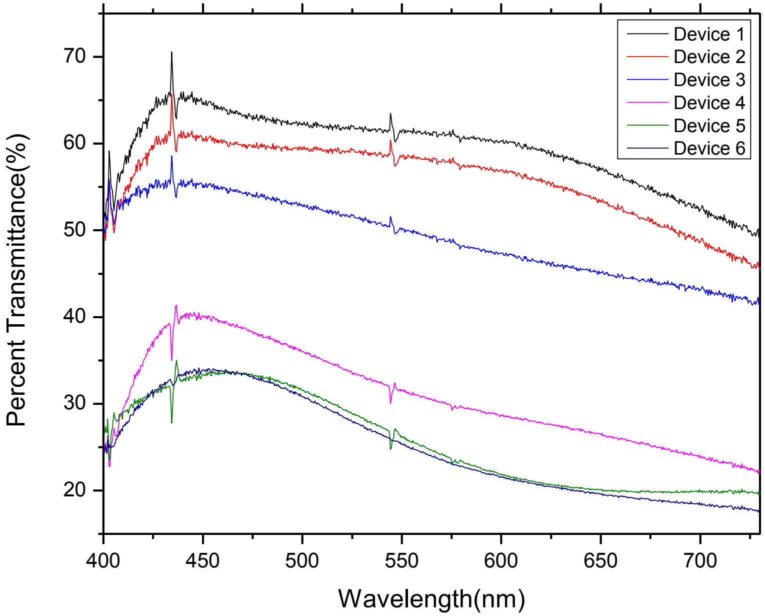


Figure : Bleached state transmittance spectra of 0.4 in^2
ECP-Black:MCCP ECDs



Device 1: Black A=1.0, MCCP A=0.5
Device 2: Black A=1.0, MCCP A=0.5
Device 3: Black A=1.0, MCCP A=0.8
Device 4: Black A=2.0, MCCP A=1.0
Device 5: Black A=2.0, MCCP A=1.0
Device 6: Black A=2.0, MCCP A=1.1

High OD ECDs-Switching kinetics of 0.4 in^2 Devices

Figure : Device 1 switching kinetics transmittance.

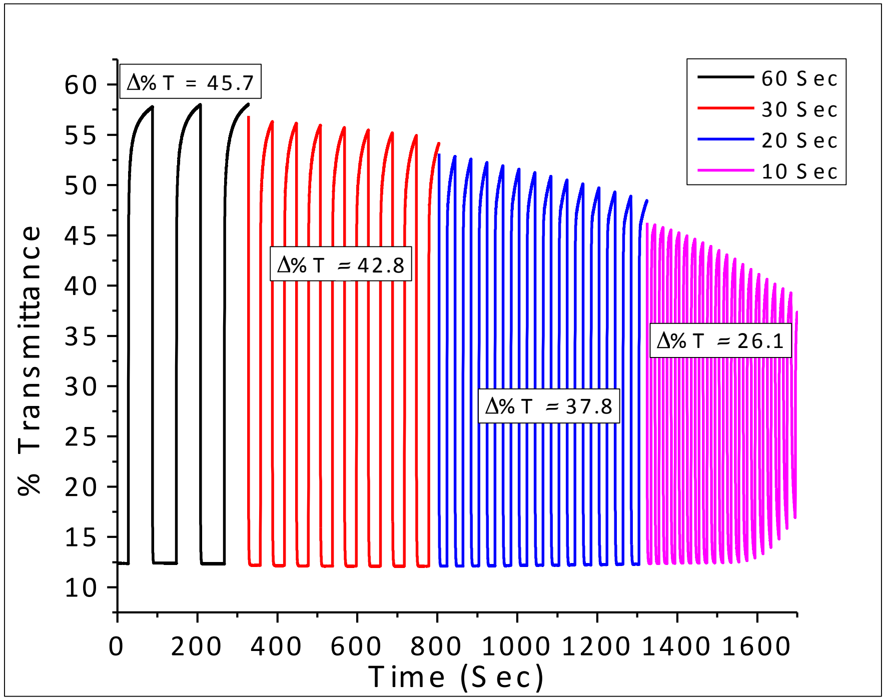
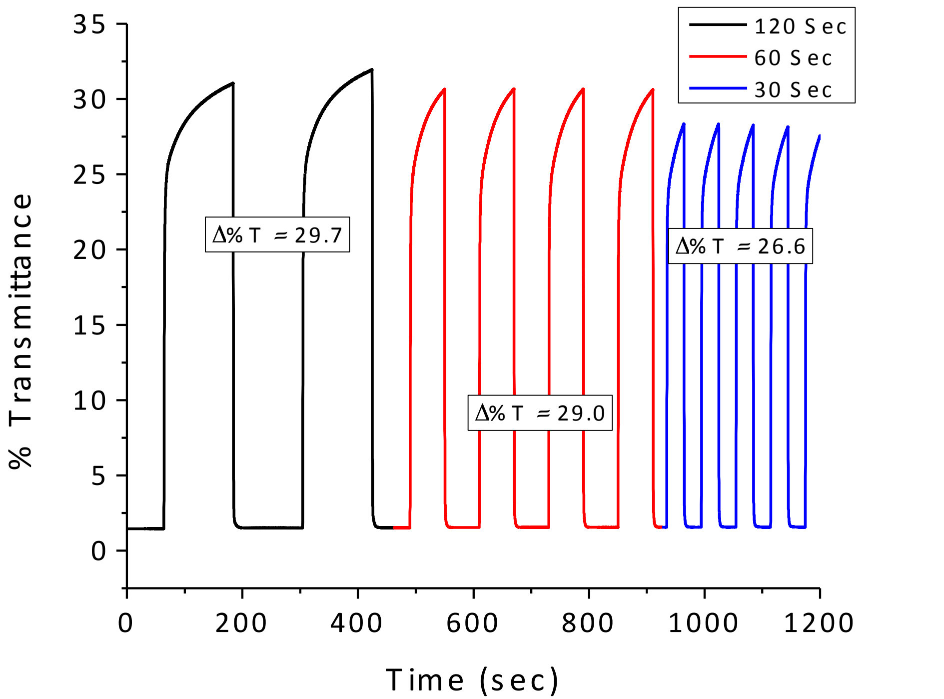


Figure : Device 4 switching kinetics transmittance.



Device 1: Black A=1.0, MCCP A=0.5
Switching from 12% to 58% T in 60 sec.
What is seen by 'eye' is much faster than monitored optically.

Device 4: Black A=2.0, MCCP A=1.0
Switching from 1.3% to 32% T in 120 sec.
Transmittance monitored at 555 nm.

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High OD ECDs-Optimization of 2.3 in^2 Devices

Status

The ideal ratio of ECP-black to MCCP (based on optical absorption at the respective polymer film λ_{max}), as found to be 2:1, was further extended to slightly larger area substrates sprayed by hand. Optical measurements that include spectral transmittance, colorimetry, lightness, and photographs and movies of the devices switching were taken.

Research Activities

Again, while the devices did not demonstrate the bleached state transmittance as-desired, the colored state transmittance was sufficiently dark. An 'irising' effect is observed in these larger devices. Further work that involves larger area electrodes should look to understand this effect and electrode engineering to lessen it through lowering of IR-drop across electrode surafce. It should be noted that a slightly higher switching voltage was required for these devices (~ +/- 2.5V)

High OD ECDs-Optimization of 2.3 in^2 Devices

Device Number	Device Abs	%T $_{580\text{-}620}$ Colored	%T$_{580\text{-}620}$ Bleached	Min %T$_{colored}$ @ 600 nm	Max %T$_{bleached}$ @ 435 nm	L* $_{colored}$	L*$_{Bleached}$
1	Black A=1.0 MCCP A=0.5	10.7	46.8	10.7	53.8	38.2	75.6
2	Black A=1.0 MCCP A=0.5	11.6	38.4	11.6	41.4	40.0	69.9
3	Black A=1.9 MCCP A=1.0	1.5	8.7	1.5	12.5	12.4	42.4
4	Black A=1.9 MCCP A=1.0	1.4	21.1	1.4	28.9	11.4	56.5

Figure : Dark state transmittance spectra of 2.3 in^2 ECP-Black:MCCP ECDs

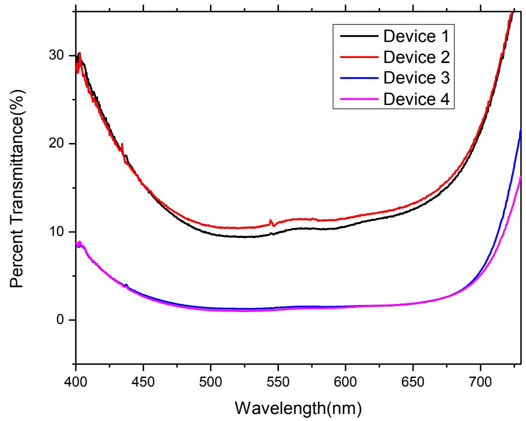
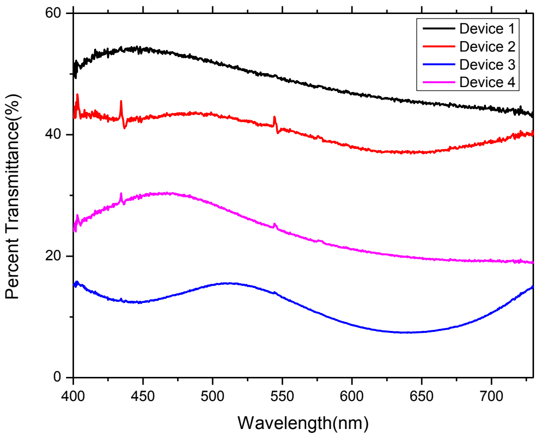


Figure : Bleached state transmittance spectra of 2.3 in^2 ECP-Black:MCCP ECDs

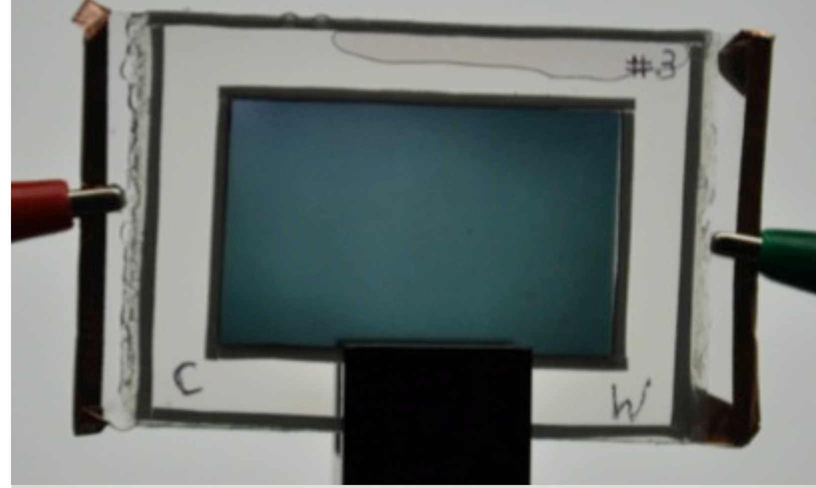


Device photographs

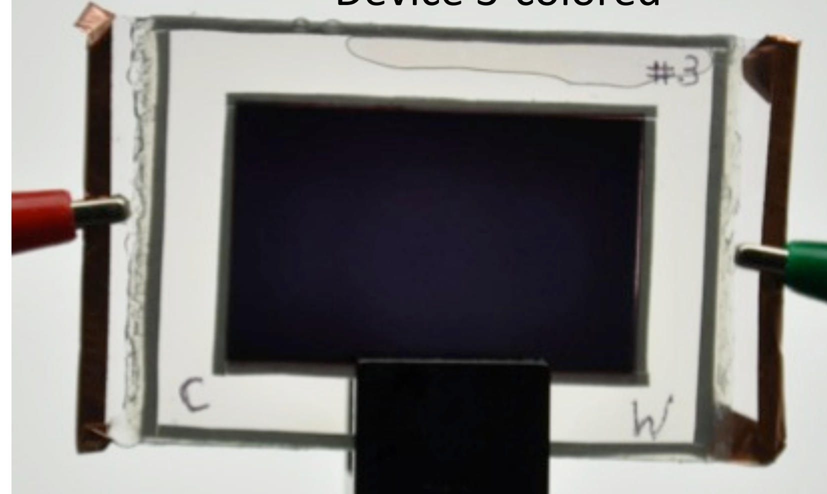
Device 2-bleached

Device 2-colored

Device 3-bleached



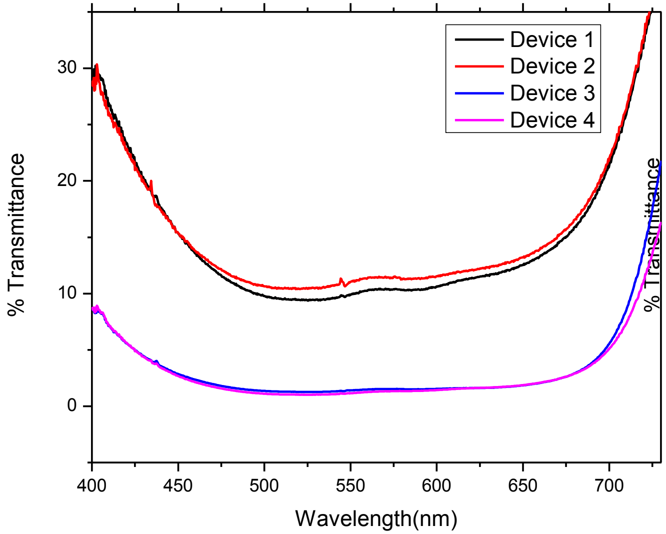
Device 3-colored



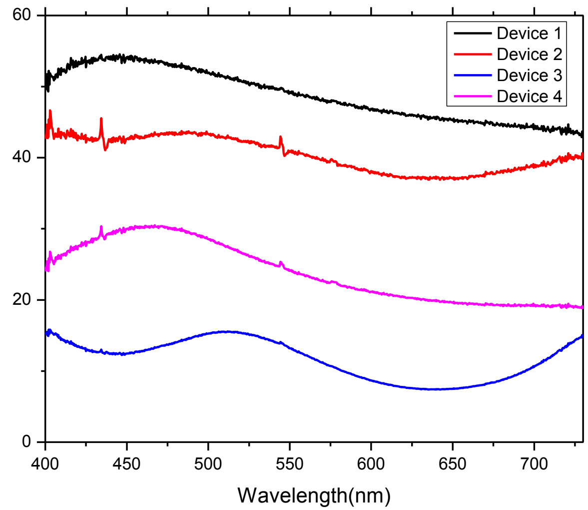
6 in^2 Dual Polymer ECP-Black/MCCP Devices

- Several devices containing ECP-Black to two different thicknesses were made of increasing size. All films were hand-sprayed and assembled

Colored



Bleached

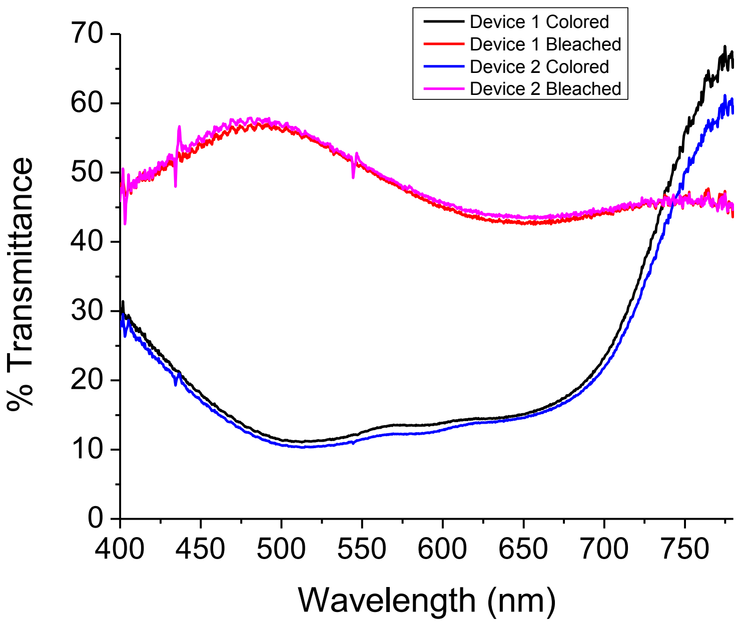


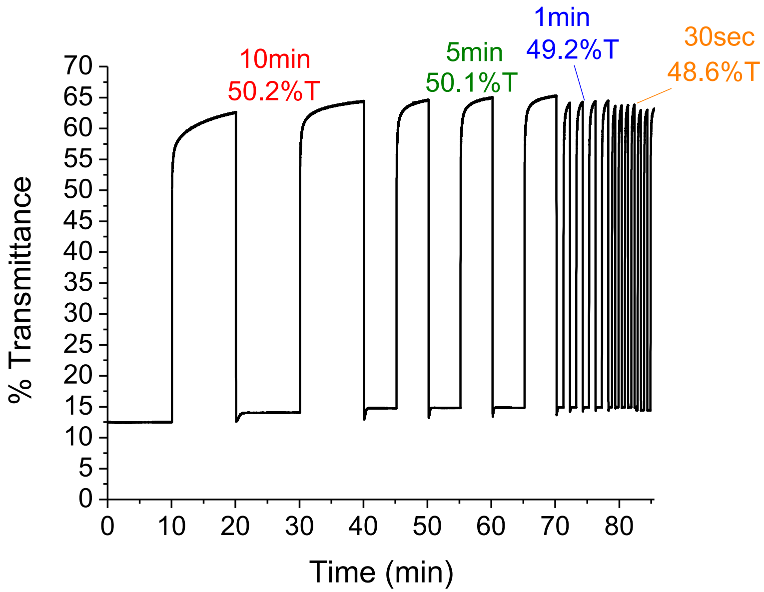
Device 2

Device	Dry Absorbance	$\%T_{550}$ Colored	$\%T_{550}$ Bleached
1	Black = 1.00	9.90	49.0
2	Black = 1.00	10.9	40.8
3	Black = 1.92	1.40	13.0
4	Black = 1.94	1.17	24.0

9 in^2 Dual Polymer ECP-Black/MCCP Devices

Device	Dry Absorbance	$\%T_{550}$ Colored	$\%T_{550}$ Bleached
1	Black = 0.91	12.6	51.1
2	Black = 0.97	11.5	50.6

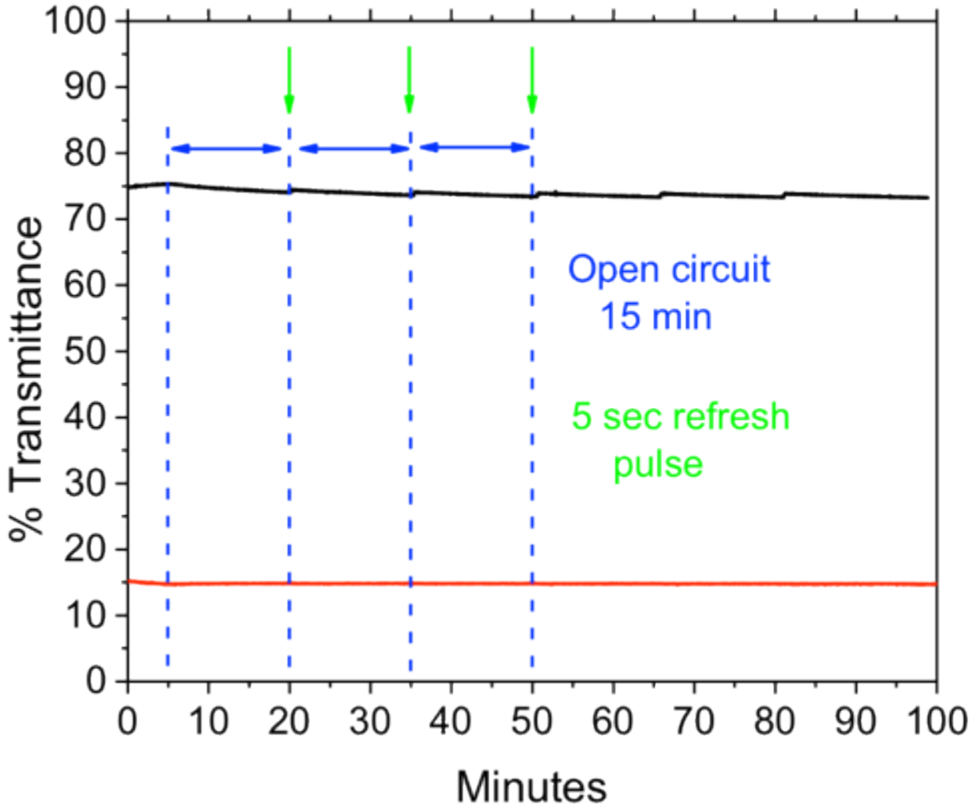




- Focus in regards to large area devices was towards using ECP-Black as the active layer to standard thicknesses (~1 a.u.).
- Devices with 9 in^2 areas exhibit similar contrast and switch speed results to the small area devices.

9 in^2 Dual Polymer ECP-Black/MCCP Devices

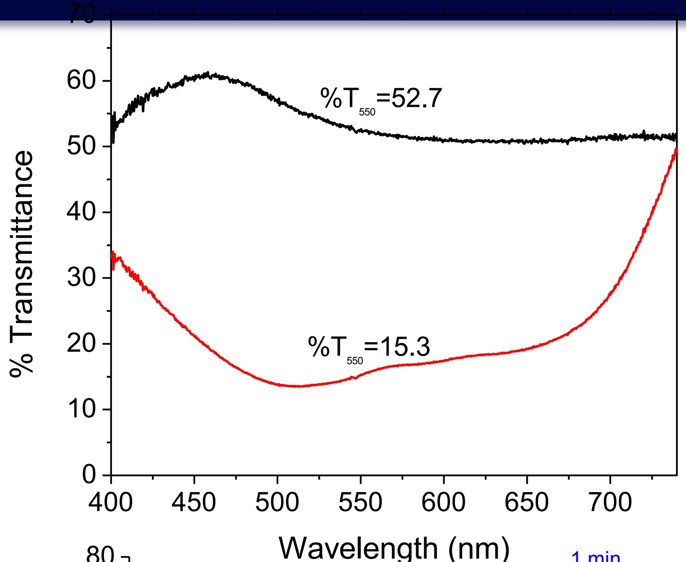
3”x3” dual polymer (ECP-black:MCCP) device

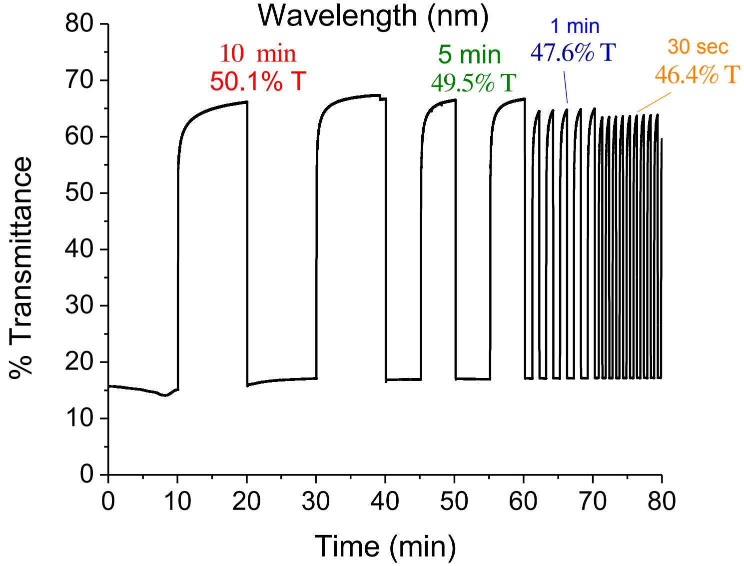


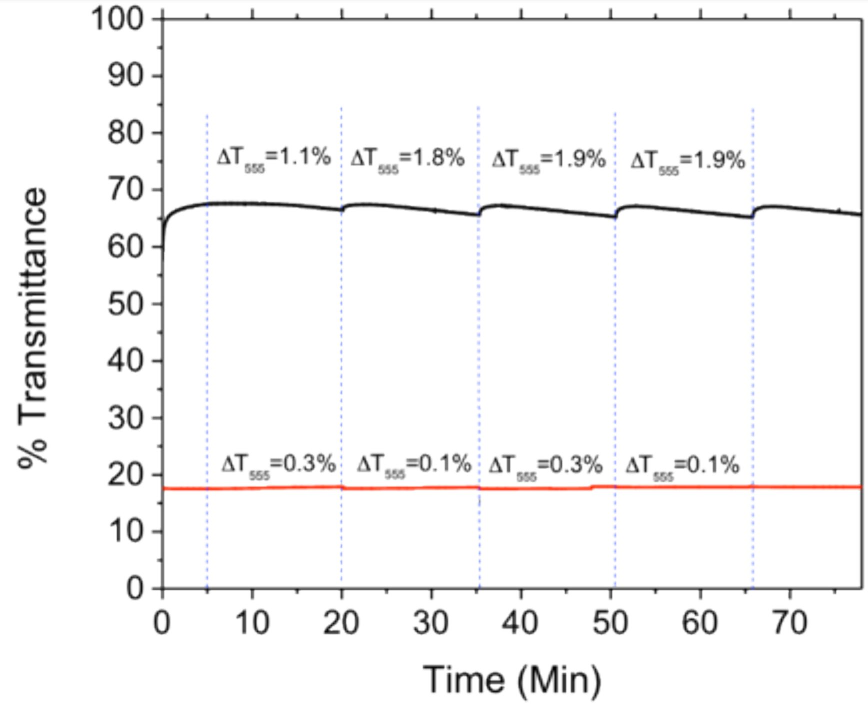
- Initial 5 min hold at +2V (bleached) or -2V (colored)
- Open circuit for 15 min.
- 5 sec refresh pulse to +/- 2V
- Open circuit again

- Bleached state dropped less than 2% from initial transmittance after 15 min open circuit
- Colored state increased less than 0.2% from initial transmittance after 15 min open circuit

16 in^2 Dual Polymer ECP-Black/MCCP Devices







- As the device area is increased further, no decrease in switch speed is seen and high level of EC memory is maintained.

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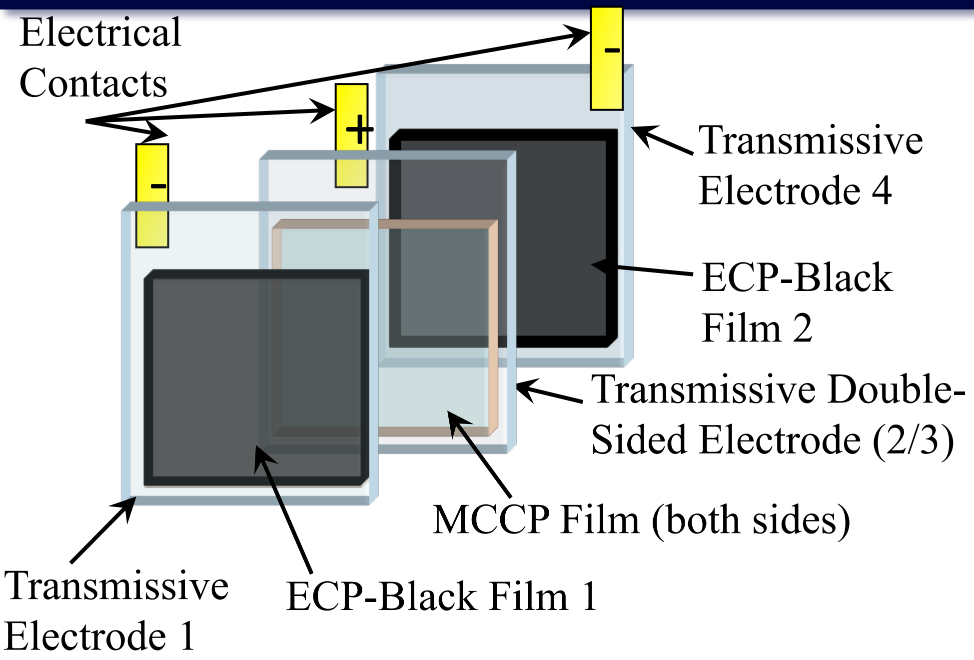
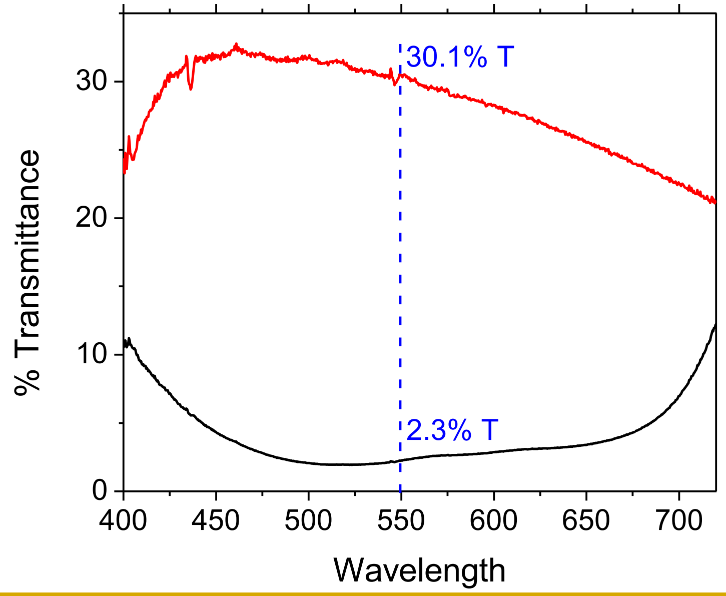
Methods to increase optical density—ECP-Black Dual-Active Devices



- Device construction with standard single-sided ITO/glass electrodes for electrodes 1 &4. Double-sided ITO/glass for electrodes 2/3.

Dual-active (stacked) polymer device (ECP-black:MCCP/ECP-black:MCCP)



- While device dark state was reached, the loss in bleached state transmittance was more than anticipated.
- Attempts to vary the thickness of the ECP-black films did not lead to the desired transmittance values.

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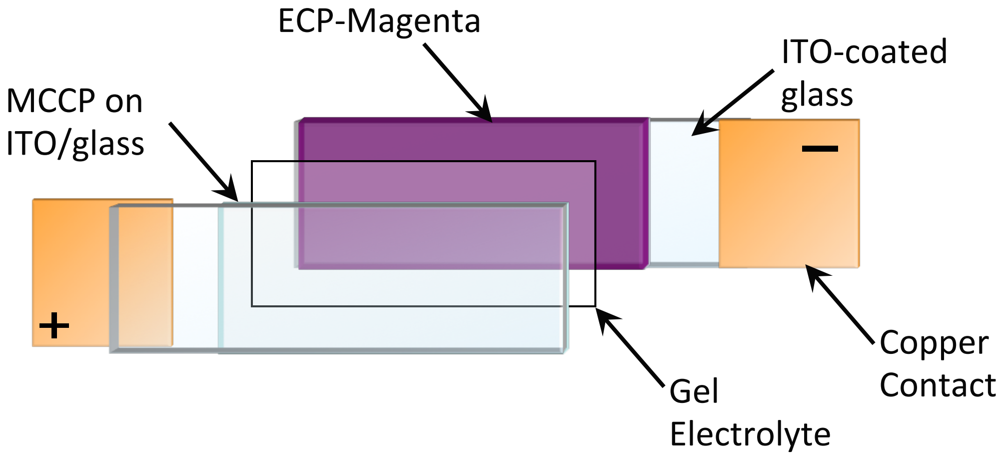
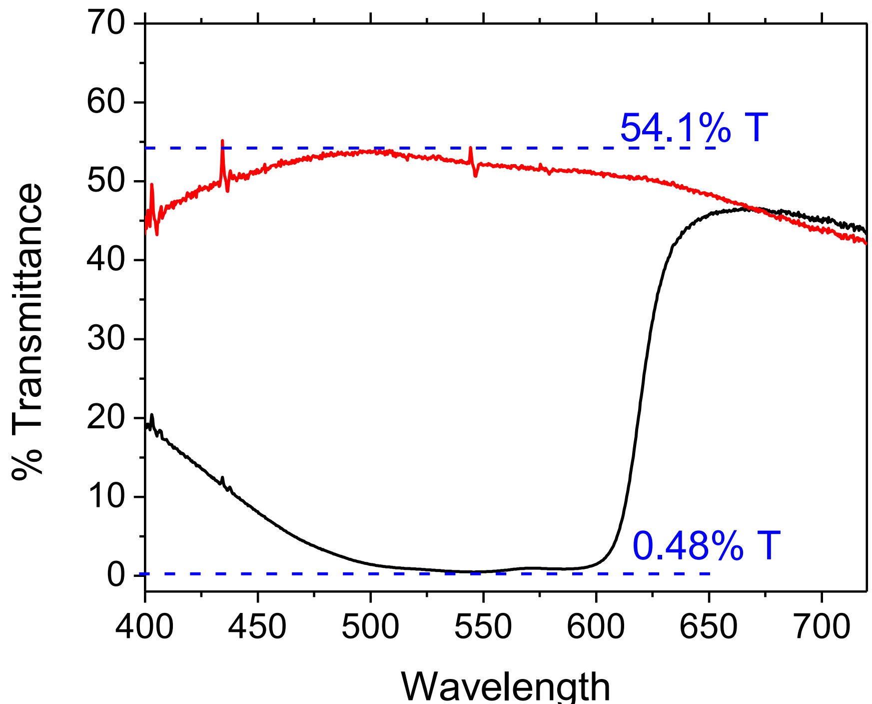
Methods to increase optical density—High Contrast Devices with ECP-Magenta

- We found that our ECP-Magenta, while not of the ideal hue for window applications, did achieve the goal transmittance values in the dark state and very close to the bleached state.

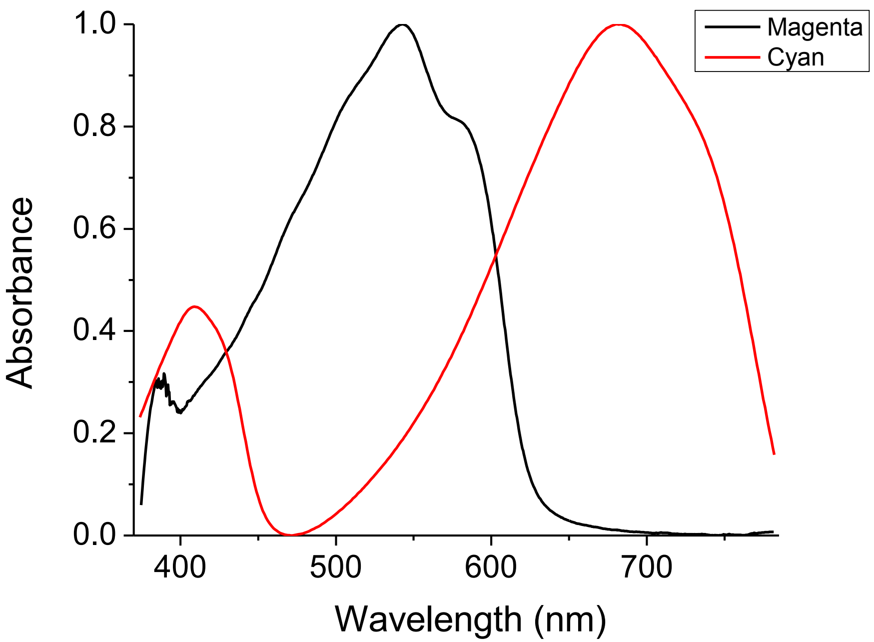




- Initial attempts to vary the ECP-Magenta film thickness produced a device that achieved ~0.5% T in the dark state and 54% T in the bleached state
- The device construction was identical to that for the ECP-black dual polymer devices.

Methods to increase optical density—High Contrast ECP-Magenta/ECP-Cyan Combinations

Individual Films of ECP-Magenta and ECP-Cyan spray-cast onto ITO/glass electrodes

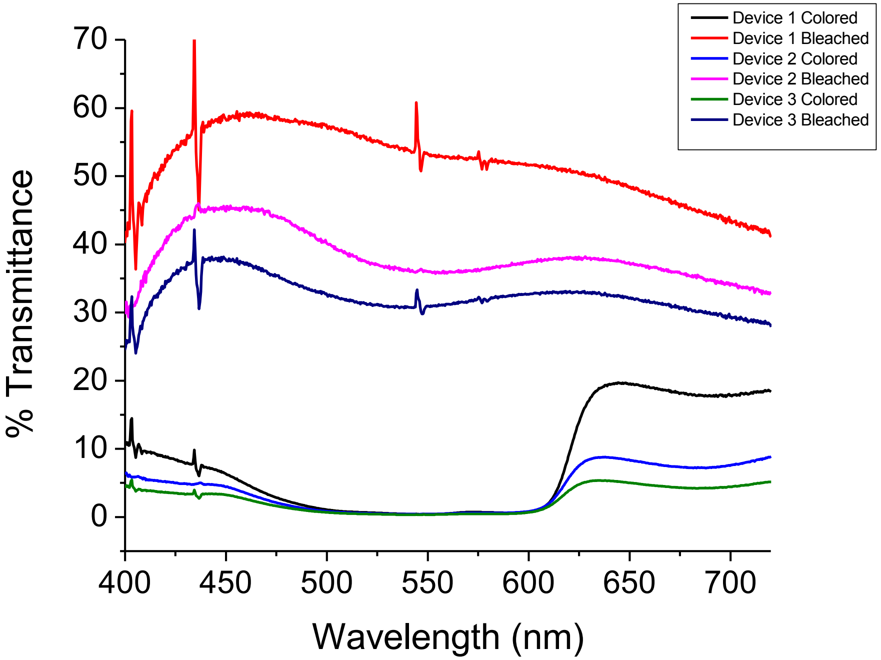


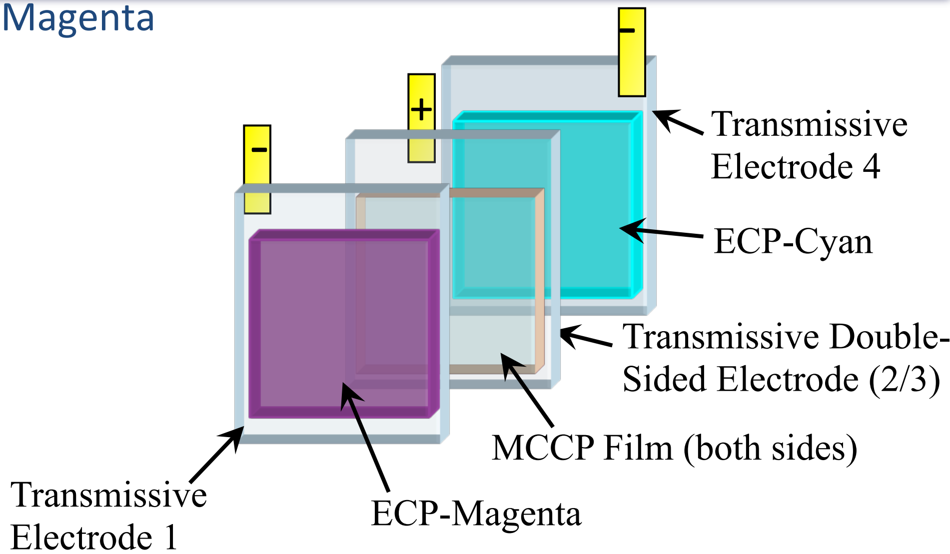
- As ECP-Magenta did not provide the broad absorption nor color desired for window applications effort was directed towards combining ECP-Magenta with a complementary polymer to broaden the absorption across the visible region.
- ECP-Cyan was chosen as it exhibited a high transmittance in the bleached state and absorbs in the low energy and high energy ends of the spectrum

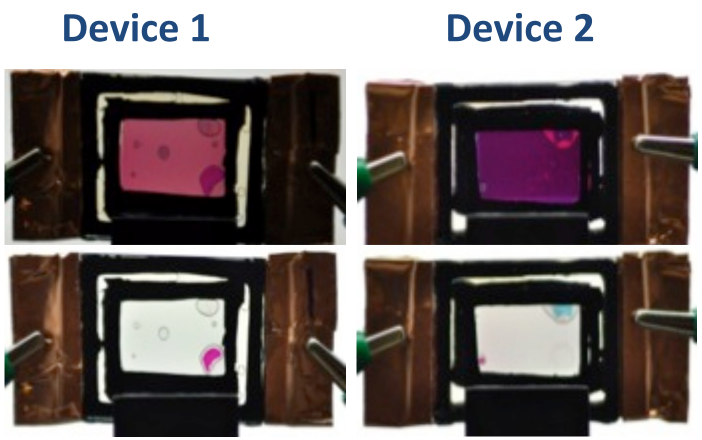
- As can be seen by the spectra to the left, ECP-Magenta absorbs broadly from 400 to 650 nm, while ECP-Cyan covers from 500 to 800.
- An approach was taken to use the dual-active device design with ECP-Magenta as one active ECP and ECP-Cyan as the other as shown above.
- Another approach was to blend the two polymers together to allow use of only two electrodes layers.

Methods to increase optical density—High Contrast ECP-Magenta/ECP-Cyan Dual-Active Devices

- Varying the relative ratios (film thicknesses) of ECP-Magenta to ECP-Cyan broadens the spectra, creating a deep purple color.







Device	Dry Film Abs	$\%T_c$	$\%T_b$	L^*_c	L^*_b	$(a^*, b^*)_c$	$(a^*, b^*)_b$
1	Magenta=1.93, Cyan=0.4	0.38	53.2	17	78	40, -23	-3, -2
2	Magenta=1.89, Cyan=0.84	0.52	36.0	11	68	28, -20	2, -8
3	Magenta=1.87, Cyan=0.96	0.36	30.8	9	63	24, -18	2, -5

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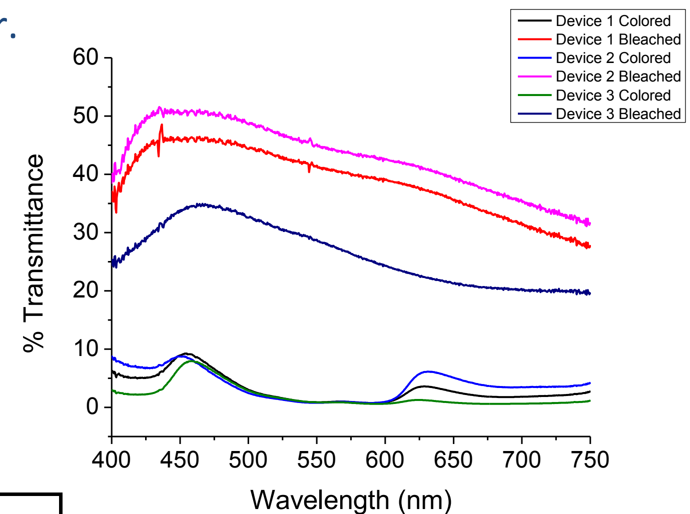
Methods to increase optical density—High Contrast ECP-Magenta/ECP-Cyan Blend Devices

Device 1

Device 2

Device 3

- Further work was towards blending the polymers and spraying a single film, eliminating 5 layers from the overall device (12 layers to 7 layers).
- Devices were constructed by blending the two polymers to different ratios and spraying as a single film. The devices contained the blended film as the active electrode and MCCP as the counter.



Device	Blend Ratio(v:v)	$\%T_c$	$\%T_b$	L^*_c	L^*_b	$(a^*, b^*)_c$	$(a^*, b^*)_b$
1	1:1(C:M)	0.9	41.0	13.9	70.3	10.8 , -29.6	-2.9 , -5.6
2	1:2(C:M)	0.8	44.6	14.3	72.8	19.3 , -29.9	-2.9 , -6.0
3	2:1(C:M)	0.9	28.1	11.8	59.8	-0.5 , -24.8	-6.9 , -6.9

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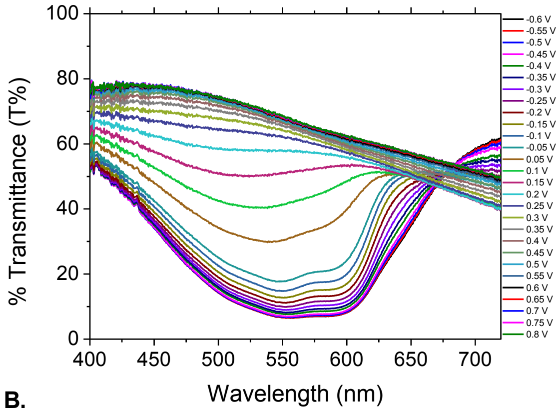
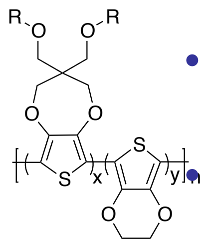
Methods to increase optical density—A New High Contrast Deep Purple ECP

- An exploratory synthesis effort was conducted to broaden the spectrum of ECP-Magenta by co-polymerizing the ProDOT-$(CH_2OEtHx)_2$ monomer with EDOT
- The result was a highly soluble polymer with a neutral spectrum that was broadened from 600 to 650 nm and a near colorless transmissive state.

A.

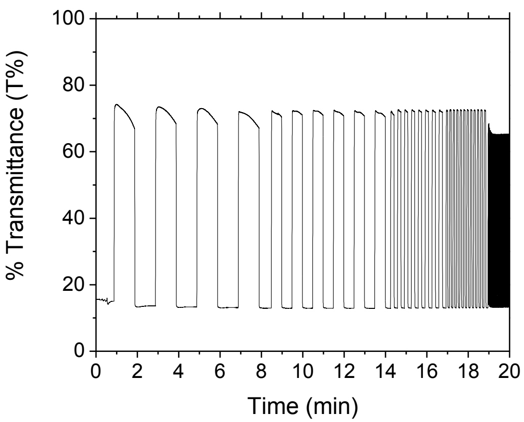




R = EtHx
x = y = 1

- Film of increasing thickness were spray-cast onto ITO/glass and characterized in a liquid electrolyte.
- The bleached state transmittance is very high with the film exhibiting a 6.6% T at 550 nm in the dark state having 68% T in the bleached state. The thickest film switched from 3%T to 56%.

B.



Dry Film Absorbance	$\%T_c$	$\%T_b$	L^*_c	L^*_b	$(a^*, b^*)_c$	$(a^*, b^*)_b$
0.95	13.7	75.8	51	89	24, -38	-3, -6
1.49	6.6	68.4	39	86	28, -44	-5, -8
1.96	2.9	55.8	28	79	30, -45	-6, -9

Georgia Tech

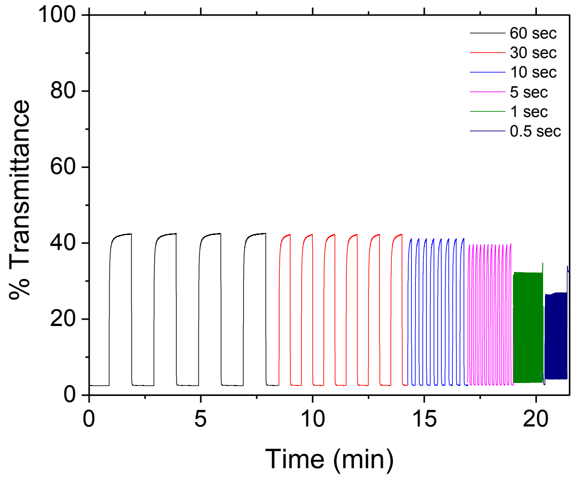
Methods to increase optical density—Devices with the New High Contrast Deep Purple ECP

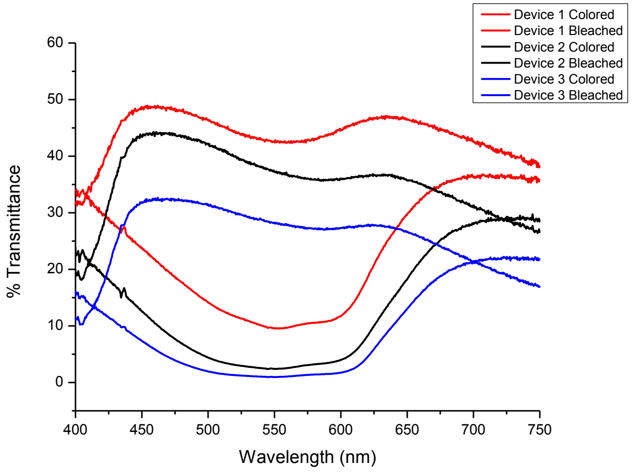
Device 1

Device 2

Device 3

Device	Dry Film Abs.	$\%T_{550}$ Colored	$\%T_{550}$ Bleached	L* Colored	L* Bleached	a*, b* Colored	a*, b* Bleached
1	1.00 a.u.	9.6	42.4	42	72	18, -23	1, -3
2	1.52 a.u.	2.4	37.2	25	68	28, -30	-3, -4
3	1.96 a.u.	1.0	28.3	16	60	29, -28	-3, -1



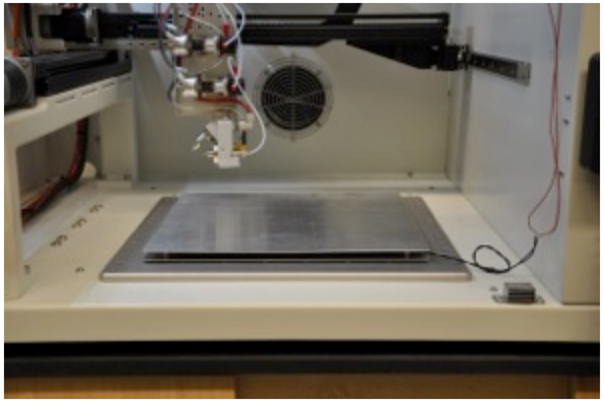


- Dual polymer ECDs containing films of increasing thickness of deep purple as the active layer and MCCP as the counter layer were constructed
- The devices exhibited near colorless bleached states as seen by the a*,b* values. However, the devices did not exhibit as high contrasts as the devices containing films of ECP-Magenta/ECP-Cyan blend.

Georgia Tech

Ultrasonic Spray-Processing—Comparison of Morphology

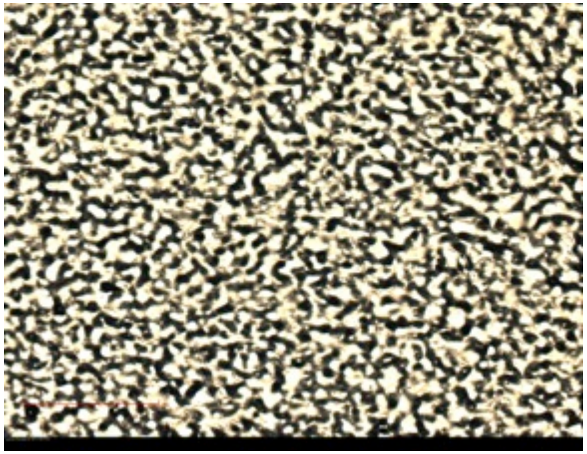
- Automated spray booth should enable better film layering, large area work and reproducible spraying
- Droplet sizes are much larger with ultrasonic spraying and have a 'pancake-like' morphology.
- The larger domains are visible to the eye with the films looking hazy.

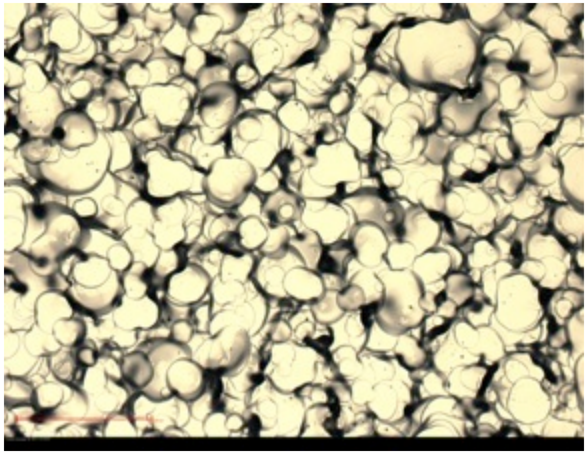


Airbrush Spraying
Solvent: Toluene

200 µm

Ultrasonic Spraying
Solvent: Toluene

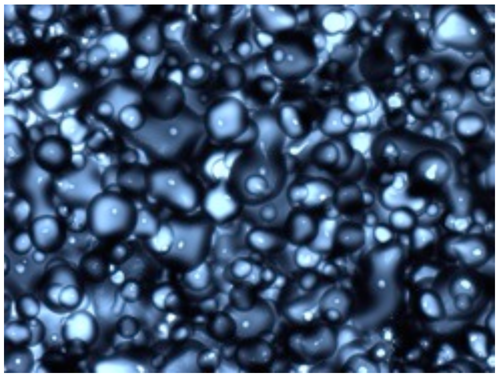




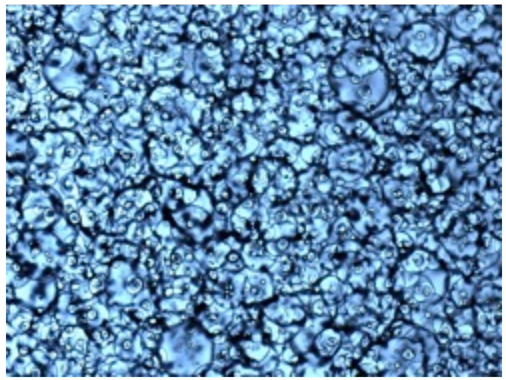
Ultrasonic Spray-Processing—Comparison of Morphology—Solvent comparisons

ECP-Black-Sonotek

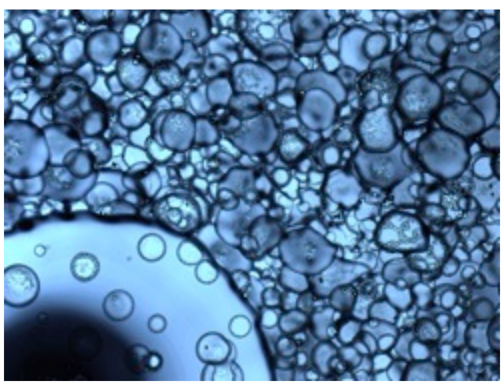
Xylenes



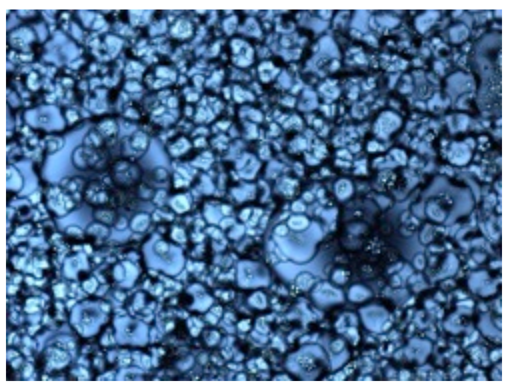
Tetrahydrofuran



Dichloromethane

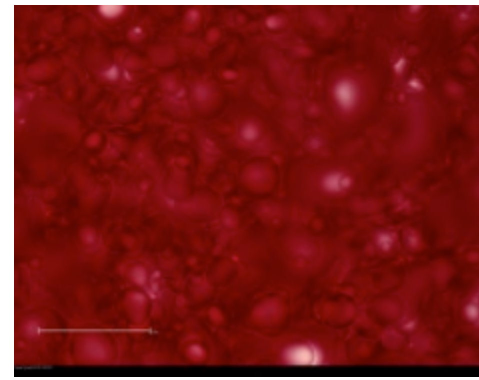


Chloroform

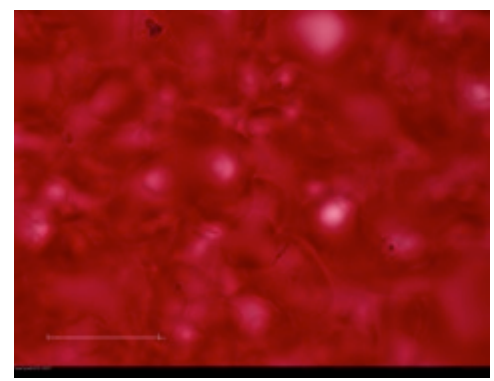


ECP-Magenta-Sonotek

Chlorobenzene

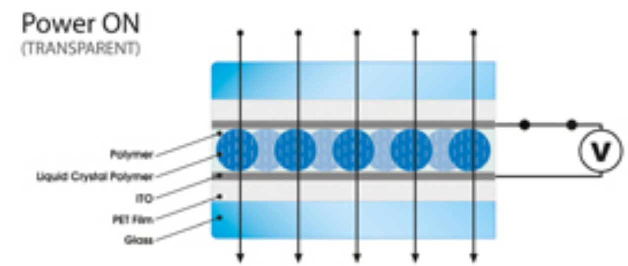


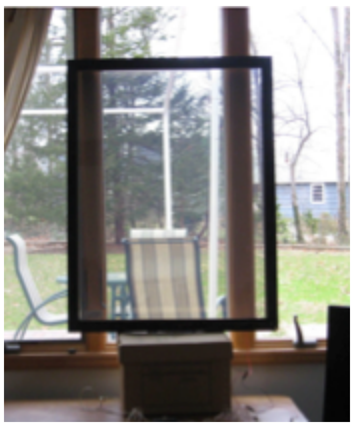
Xylenes



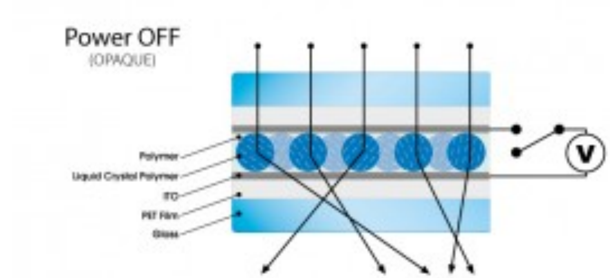
Limitations and Opportunities for High OD Windows—Coupling ECDs to other technologies

LC SmartGlass
1 sec on/off
100Vac
Vis Transmission: 75% to 67%
Clarity: 76% to 4%





SPD Control Systems
Switching in seconds
Vac required
Vis Transmission <1% to >50%



Electrochromics may not allow for highest optical density while reaching level of transmittance needed in bleached state for Aerospace applications. While other technologies (as shown above, require high voltages or only scatter light. There is promise by coupling light scattering technology (to block largest amount of light) to ECDs (to absorb remaining light). ECDs may also allow low power light filtering when shaded (but not blocked) conditions needed.